

OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-91-J-1630

PR Number 96PR00670

Creation and Measurement of Components for Nanometer-Scale and Hybrid-Function Devices

Paul S. Weiss

Department of Chemistry
The Pennsylvania State University

152 Davey Laboratory
University Park, PA 16802-6300

Date Submitted
27 February 1999

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Office of Naval Research Final Report

Reporting period:
1 January 1997 to 31 December 1999
PR Number: 96PR00670

20001208 030

Final Report - PART I

a. *Papers submitted to refereed journals, but not yet published:*

TR 29. *Enhancing Catalytic Reactions by Aligning Reactive Intermediates: Phenyl on Cu{111}, M. M.*

DTIC QUALITY IMPROVED 4

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 2/27/00		2. REPORT DATE TYPE Final		3. DATES COVERED (From - To) 1/1/97-12/31/99	
4. TITLE AND SUBTITLE Creation and Measurement of Components for Nanometer-Scale and Hybrid-Function Devices				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER N00014-91-J-1630	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Paul S. Weiss				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Pennsylvania State University University Park, PA 16802				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. John Pazik Chemistry Division Office of Naval Research 800 N. Quincy St., Code 1113 Arlington, VA 22217				10. SPONSOR/MONITOR'S ACRONYM(S) ONR	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT See attached.					
15. SUBJECT TERMS Directed assembly Nanotechnology Scanning probe spectroscopy Hierarchical structures Local probes Hierarchical assemblies Scanning probe microscopy					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code)

14. Abstract

We have learned to manipulate defects, domains, crystallinity, desorption, exchange, insertion, grafting, conductance, and deposition to advantage in order to manipulate film structures and properties and to isolate molecules for use, study, and/or reaction.

We have enhanced our abilities to measure with sub-nanometer resolution across a broad spectral range. We have discovered unique opportunities at this scale, such as "optically hot" asperities on asymmetric nanoparticles. We expect to be able to exploit these effects to advantage. There are no other means of studying such materials at these scales. Couplings between molecules and nanoparticles that we propose to study may pose fundamental limitations on the densities to which functional devices can be packed.

We have demonstrated our ability to discriminate between different nanostructure compositions. We have proposed using this capability to develop selective "stains" for scanning probe microscopy in analogy to those employed in conventional light microscopy. The difference here is that much higher spatial resolution will be possible so that single exposed functional groups may be labeled.

Kamna, T. M. Graham, and P. S. Weiss, submitted for publication.

TR 30. *The Effects of Steps and Substrate-Mediated Interactions on Langmuir-Hinshelwood Reaction Rates*, E. N. Schulman and P. S. Weiss, submitted for publication.

TR 58. *Local Electronic Structural Effects and Measurements on the Adsorption of Benzene of Ag{110}*, J. I. Pascual, J. J. Jackiw, K. F. Kelly, H. Conrad, H.-P. Rust, and P. S. Weiss, submitted for publication.

Note that a number of other manuscripts based on ONR-supported work are in preparation on self-assembly, directed assembly, nanoparticle assemblies and spectroscopy, and functional molecules.

b. *Papers published in refereed journals:*

TR 28. *Surface Characterization*, G. E. McGuire,* P. S. Weiss, J. G. Kushmerick, J. A. Johnson, S. J. Simko, R. J. Nemanich, N. R. Parikh, and D. R. Chopra, *Analytical Chemistry* **69**, 231R (1997).

TR 31. *Imaging Benzene and Phenyl on Cu{111}*, P. S. Weiss, M. M. Kamna, T. M. Graham, and S. J. Stranick, *Langmuir* **14**, 1284 (1998).

TR 32. *Insertion, Conductivity, and Structures of Single and Bundled Conjugated Organic Oligomers in Self-Assembled Alkanethiol Monolayers on Au{111}*, M. T. Cygan, L. A. Bumm, J. J. Arnold, N. F. Shedlock, T. D. Dunbar, T. Burgin, D. L. Allara, J. M. Tour, and P. S. Weiss, *Journal of the American Chemical Society* **120**, 2721 (1998).

TR 33. *Design, Operation, and Housing of an Ultrastable, Low Temperature, Ultrahigh Vacuum Scanning Tunneling Microscope*, J. H. Ferris, J. G. Kushmerick, J. A. Johnson, R. B. Kessinger, H. F. Kingsbury, M. G. Yoshikawa Youngquist, and P. S. Weiss, *Review of Scientific Instruments* **69**, 2691 (1998).

TR 34. *Creating, Tailoring and Using One-Dimensional Interfaces in Two-Dimensional Films*, P. S. Weiss, H. Yokota, R. Aebersold, G. van den Engh, L. A. Bumm, J. J. Arnold, T. D. Dunbar, and D. L. Allara, *Journal of Physics: Condensed Matter* **10**, 7703 (1998).

TR 35. *Directed Self-Assembly to Create Molecular Terraces with Molecularly Sharp Boundaries in Organic Monolayers*, L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, *Journal of the American Chemical Society* **121**, 8017 (1999).

TR 36. *Electron Transport through Organic Molecules*, L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, *Journal of Physical Chemistry B* **103**, 8122 (1999).

TR 38. *Probing Electronic Properties of Conjugated and Saturated Molecules in Self-Assembled Monolayers*, P. S. Weiss, L. A. Bumm, T. D. Dunbar, T. P. Burgin, J. M. Tour, and D. L. Allara, *Annals of the New York Academy of Sciences* **852**, 145 (1998).

TR 39. *Evolution of Strategies for Self-Assembly and Hookup of Molecule-Based Devices*, D. L. Allara, T. D. Dunbar, P. S. Weiss, L. A. Bumm, M. T. Cygan, J. M. Tour, W. A. Reinert, Y. Yao, M. Kozaki, and L. Jones, II, *Annals of the New York Academy of Sciences* **852**, 349 (1998).

TR 41. *Strong Electronic Perturbation of the Cu{111} Surface by 7,7',8,8'-Tetracyanoquinodimethane*,

- M. M. Kamna, T. M. Graham, J. C. Love, and P. S. Weiss, *Surface Science* **419**, 12 (1998).
- TR 42. *Mobile Promoters on Anisotropic Catalysts: Ni on MoS₂*, J. G. Kushmerick and P. S. Weiss, *Journal of Physical Chemistry B* **102**, 10094 (1998).
- TR 43. *Molecular Motion to Step Edges*, J. H. Ferris, J. G. Kushmerick, and P. S. Weiss, *Surface Science* **446**, 112 (2000).
- TR 44. *Spatially Resolved Spectroscopic Analysis: Scanning Probe Microscopies*, J. G. Kushmerick and P. S. Weiss, *Encyclopedia of Spectroscopy and Spectrometry*, G. Tranter and J. Holmes, eds. (Academic Press, London, 2000), in press.
- TR 45. *Scanning Probe Studies of Single Nanostructures*, G. S. McCarty and P. S. Weiss, *Chemical Reviews* **99**, 1983 (1999).
- TR 46. *Observations of Anisotropic Electron Scattering on Graphite with a Low Temperature Scanning Tunneling Microscope*, J. G. Kushmerick, K. F. Kelly, N. J. Halas, H. P. Rust, and P. S. Weiss, *Journal of Physical Chemistry B* **103**, 1619 (1999).
- TR 47. *Ring-Opening Metathesis Polymerization from Surfaces*, M. Weck, J. J. Jackiw, R. R. Rossi, P. S. Weiss, and R. H. Grubbs, *Journal of the American Chemical Society* **121**, 4088 (1999).
- TR 48. *Formation of Nanoscale Polarized Domains in Organic Ferroelectric Thin Films by Scanning Force Microscopy*, X. Q. Chen, H. Yamada, T. Horiuchi, K. Matsushige, and P. S. Weiss, *Molecular Crystals and Liquid Crystals A* **337**, 285 (1999).
- TR 49. *Scanning Tunneling Microscopy and Spectroscopies of Nanometer-Scale Particles*, G. S. McCarty, J. C. Love, J. G. Kushmerick, L. F. Charles, C. D. Keating, B. J. Toleno, M. E. Lyn, A. W. Castleman, Jr., M. J. Natan, and P. S. Weiss, *Journal of Nanoparticle Research* **1** (1999), in press.
- TR 50. *Surface Characterization*, G. E. McGuire, D. J. Fuchs, P. Han, J. G. Kushmerick, P. S. Weiss, R. J. Nemanich, N. R. Parikh, and D. R. Chopra, *Analytical Chemistry* **71**, 373R (1999).
- TR 51. *Strong Substrate Effect in Local Poling of Ultrathin Ferroelectric Polymer Films*, X. Q. Chen, Y. Terai, T. Horiuchi, H. Yamada, K. Matsushige, and P. S. Weiss, *Thin Solid Films* **353**, 259 (1999).
- TR 52. *Surface Potential of Ferroelectric Thin Films Investigated by Scanning Probe Microscopy*, X. Q. Chen, H. Yamada, T. Horiuchi, K. Matsushige, S. Watanabe, M. Kawai, and P. S. Weiss, *Journal of Vacuum Science and Technology B* **17**, 1930 (1999).
- TR 53. *Combined Scanning Tunneling Microscopy and Infrared Spectroscopic Characterization of Mixed Surface Assemblies of Linear Conjugated Guest Molecules in Host Alkanethiolate Monolayers on Gold*, T. D. Dunbar, M. T. Cygan, L. A. Bumm, G. S. McCarty, T. P. Burgin, J. J. Jackiw, J. M. Tour, P. S. Weiss, and D. L. Allara, *Journal of Physical Chemistry B*, in press.
- TR 57. *Atomic-Scale Insights into Hydrodesulfurization*, J. G. Kushmerick, S. A. Kandel, P. Han, J. A. Johnson, and P. S. Weiss, *Journal of Physical Chemistry B*, in press.
-

c. Books or chapters submitted, but not yet published:

None.

d. Books or chapters published:

None.

e. Printed technical reports/non-refereed papers:

TR 37. *Self-Assembled Monolayer Formation of Organoselenium Compounds on Gold and its Significance for Molecular Scale Electronics*, W. A. Reinerth, T. P. Burgin, T. D. Dunbar, L. A. Bumm, J. J. Arnold, J. J. Jackiw, C. Zhou, M. R. Deshpande, D. L. Allara, P. S. Weiss, M. A. Reed, and J. M. Tour, *Proceedings of Polymer Materials, Science, and Engineering (American Chemical Society, Division of Polymer Materials Science and Engineering)* **78**, 178 (1998).

TR 40. *Ring-Opening Metathesis Polymerization from Surfaces*, M. Weck, J. J. Jackiw, P. S. Weiss, and R. H. Grubbs, *Proceedings of Polymer Materials, Science, and Engineering (American Chemical Society, Division of Polymer Materials Science and Engineering)* **79**, 72 (1998).

TR 54. *Molecular Scale Electronics*, A. M. Rawlett, E. T. Mickelson, W. A. Reinerth, L. Jones II, M. Kozaki, T. P. Burgin, J. M. Tour, J. Chen, C.-W. Zhou, C. J. Muller, M. R. Deshpande, M. A. Reed, L. A. Bumm, M. T. Cygan, T. D. Dunbar, P. S. Weiss, and D. L. Allara, *Proceedings of the Materials Research Society*, in press.

TR 55. *Molecular Scale Electronics. Critical Nanolithography Issues of Synthesis and Addressing*, S. Huang, E. T. Mickelson, A. M. Rawlett, C. L. Asplund, A. M. Cassell, M. Kozaki, T. P. Burgin, L. Jones, II, J. M. Tour, M. L. Myrick, P. G. van Patten, J. Chen, C.-W. Zhou, C. J. Muller, M. R. Deshpande, M. A. Reed, L. A. Bumm, M. T. Cygan, T. D. Dunbar, P. S. Weiss, and D. L. Allara, *Proceedings of the Materials Research Society*, in press.

TR 56. *Bulk Production, Isolation, and Characterization of Metallocarbohedrenes*, M. E. Lyn, G. S. McCarty, D. E. Bergeron, E. R. Statz, A. D. Korman, P. S. Weiss, and A. W. Castleman, Jr., submitted to *Cluster and Nanostructure Interfaces, Proceedings of the International Symposium*, Richmond, Virginia, USA 25 - 28 October 1999, P. Jena, S. N. Khanna, and B. K. Rao, eds. (World Scientific Press, Singapore, 2000), in press.

f. Patents filed:

None.

g. Patents granted:

None.

h. Invited presentations:

National Security Agency, Microelectronics Research Laboratory, "Probing and Manipulating Single Atoms and Molecules," P. S. Weiss, Columbia, MD, January 28, 1997.

213th Meeting of the American Chemical Society, "Surface Chemistry: Following Brian Bent," P. S. Weiss, Brian Bent Memorial Symposium, San Francisco, CA, April 15, 1997.

213th Meeting of the American Chemical Society, "Probing Single Molecules with Scanning Tunneling Microscopy," P. S. Weiss, San Francisco, CA, April 16, 1997.

University of Oregon, Materials/Physical Chemistry and Condensed Matter Physics Seminar, Departments of Chemistry and Physics, "Atomic-Scale Views of Coupled Interactions and Dynamics on Surfaces," P. S. Weiss, Eugene, OR, April 18, 1997.

University of Chicago, Department of Chemistry Colloquium, "Atomic-Scale Views of Interactions and Dynamics of Single Molecules on Surfaces," P. S. Weiss, Chicago, IL, May 5, 1997.

University of Pennsylvania, Physical Chemistry Seminar, Department of Chemistry, "Atomic-Scale Views of Interactions and Dynamics of Molecules on Surfaces," P. S. Weiss, Philadelphia, PA, May 8, 1997.

University of Washington, Department of Chemistry and Physics, "Atomic-Scale Views of Interactions and Dynamics of Molecules on Surfaces," P. S. Weiss, Seattle, WA, May 12, 1997.

Charles Evans and Associates, "Atomic-Scale Views of Atoms and Molecules on Surfaces," P. S. Weiss, Redwood City, CA, May 14, 1997.

University of Washington, Department of Molecular Biotechnology, Science in Progress Seminar, "Marrying Techniques for Manipulating and Probing Single Molecules: Something Old, Something New, Something Borrowed, Something Blue" P. S. Weiss, Seattle, WA, May 28, 1997.

JASON, "Genomic Technologies," P. S. Weiss, La Jolla, CA, July 3, 1997.

Eighth International Conference on Organized Molecular Films, "Control of the Structure and Properties of Self-Assembled Monolayers," P. S. Weiss, Pacific Grove, CA, August 24-29, 1997.

214th Meeting of the American Chemical Society, "Patterning Molecules on the Nanometer Scale," P. S. Weiss, J. J. Arnold, L. A. Bumm, L. F. Charles, M. T. Cygan, T. D. Dunbar, and D. L. Allara, Las Vegas, NV, September 8, 1997.

214th Meeting of the American Chemical Society, "Combining IR Spectroscopy and STM for Probing Inserted Molecules in Monolayer Assemblies," D. L. Allara, P. S. Weiss, T. D. Dunbar, M. T. Cygan, J. Arnold and L. A. Bumm, Las Vegas, NV, September 10, 1997. Presented by D. L. Allara.

International Workshop on Surface Chemistry on the Nanoscopic Scale, "Natural and Artificial Means of

Controlling Molecules on Surfaces," P. S. Weiss, Oegstgeest, The Netherlands, September 13, 1997.

International Conference on Molecular Electronics -- Science and Technology, "Electron Transport through Organic Molecules Isolated or Organized in Monomolecular Films" P. S. Weiss, Palmas del Mar, Puerto Rico, December 15, 1997.

International Conference on Molecular Electronics -- Science and Technology, "Strategies for Self-Assembly And Hookup of Molecule-Based Devices" D. L. Allara, T. Dunbar, P. S. Weiss, L. A. Bumm, M. T. Cygan, Palmas del Mar, Puerto Rico, December 16, 1997.

Society of Analytical Chemists of Pittsburgh, Pittsburgh, "Single Molecules in Chemistry and Biology" P. S. Weiss, Philadelphia, PA, January 12, 1998.

DARPA Workshop on the Status and Future of Molecular Electronics, "Probing Molecular Electronics and Photonics at the Nanometer Scale: Capabilities and Directions," P. S. Weiss, Reston, VA, February 3, 1998.

American Association for the Advancement of Science Annual Meeting and Science Innovation Symposium, "Manipulating and Probing Single Molecules in Chemistry, Physics, and Bioogy," Philadelphia, PA, P. S. Weiss, Philadelphia, PA, February 13, 1998.

215th Meeting of the American Chemical Society, "Patterning Molecules on the Nanometer Scale," P. S. Weiss, J. J. Arnold, L. A. Bumm, L. F. Charles, M. T. Cygan, T. D. Dunbar, and D. L. Allara, Dallas, TX, March 30, 1998.

Kyoto University, Venture Business Laboratory, Department of Electronic Science and Engineering, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Kyoto, Japan, August 5, 1998.

MITRE/DARPA Annual Meeting on Nanometer-Scale Control and Devices, "Current and Future Experimental Developments in Molecular Electronics," J. C. Love, G. S. McCarty, C. D. Keating, M. J. Natan, and P. S. Weiss, Reston, VA, August 13, 1998. Presented by J. C. Love.

216th Meeting of the American Chemical Society, "Measuring and Understanding Electron Transport Through Molecules Isolated or Organized in Monomolecular Films," P. S. Weiss, Boston, MA, August 23, 1998.

Tohoku University, Institute for Materials Research, "Electrons In, Around, and Through Molecules on Surfaces," P. S. Weiss, Sendai, Japan, September 5, 1998.

Osaka University, Institute for Scientific and Industrial Research, "Electrons In, Around, and Through Molecules on Surfaces," P. S. Weiss, Osaka, Japan, September 8, 1998.

RIKEN, Institute for Physical and Chemical Research, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Wako-shi, Saitama, Japan, September 21, 1998.

Joint Research Center for Atom Technology and the National Institute for Advanced Interdisciplinary Research, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Tsukuba, Ibaraki, Japan, September 22, 1998.

25th Annual Conference of the Federation of Analytical Chemistry & Spectroscopy Societies, P. S. Weiss,

Austin, TX, October 12, 1998.

University of California at San Diego, Department of Chemistry, "Electrons In, Around, and Through Molecules on Surfaces," P. S. Weiss, La Jolla, CA, October 13, 1998.

The Pennsylvania State University, Department of Physics, "Electrons In, Around, and Through Molecules on Surfaces," P. S. Weiss, University Park, PA, October 29, 1998.

IBM T. J. Watson Research Center, Nanotechnology Seminar, "Electrons In, Around, and Through Molecules on Surfaces," P. S. Weiss, Yorktown Heights, NY, November 18, 1998.

Lucent Technologies, Bell Laboratories, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Murray Hill, NJ, November 19, 1998.

Yale University, Department of Electrical Engineering, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, New Haven, CT, November 20, 1998.

National Institute of Standards and Technology, "Probing the Atomic-Scale Chemistry and Physics of Anisotropic Surfaces," J. G. Kushmerick, December 15, 1998.

International Workshop on Electron Transmission through Molecular Interfaces, "Electrons In, Around, and Through Adsorbed Molecules," P. S. Weiss, Sea of Galilee, Israel, December 16, 1998.

JRCAT Workshop on Technology for Identifying and Manipulating Atoms & Molecules, The 2nd Workshop on Scanning Probe and Nanoelectronics (SP-Nano '99), and the 3rd Asian Conference on Scanning Tunneling Microscopy (Asian STM '99) "Selectively Placing Molecules in Monolayer Films through Self-Assembly and Directed Assembly," P. S. Weiss, Tsukuba, Ibaraki, Japan, January 13, 1999.

University of Delaware, Department of Chemistry, "Probing the Atomic-Scale Chemistry and Physics of Anisotropic Surfaces," J. G. Kushmerick, Newark, DE, February 12, 1999.

Holy Cross, Department of Chemistry, "Molecular Measurements with Scanning Tunneling Microscopy," Lloyd A. Bumm, Worcester, MA, February 19, 1999.

University of California at Berkeley, Department of Chemistry and the Lawrence Berkeley Laboratory, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Berkeley, CA, March 4, 1999.

IBM Almaden Research Center, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, San Jose, CA, March 5, 1999.

University of California at Santa Barbara, Department of Chemistry, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Santa Barbara, CA, March 8, 1999.

Sandia National Laboratory, "Probing the Atomic-Scale Chemistry and Physics of Anisotropic Surfaces," J. G. Kushmerick, Albuquerque, NM, April 12, 1999.

Los Alamos National Laboratory, "Probing the Atomic-Scale Chemistry and Physics of Anisotropic Surfaces," J. G. Kushmerick, Los Alamos, NM, April 14, 1999.

National Institute of Standards and Technology, "Exploring and Controlling the Atomic-Scale World," P.

S. Weiss, Gaithersburg, MD, June 18, 1999.

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Surface Physics, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Berlin, Germany, June 21, 1999.

Delft University of Technology, Department of Applied Physics, "Exploring and Controlling the Atomic-Scale World," P. S. Weiss, Delft, The Netherlands, June 23, 1999.

STM '99: the 10th Scanning Tunneling Microscopy Conference, "Controlling the Placement of Molecules in the Self-Assembly and Directed Assembly of Organic Monolayers," P. S. Weiss, Seoul, Korea, July 20, 1999.

Single Molecules - Tools and Techniques for Analyses and Applications, "Probing Single Molecular Electronics and Chemistry at the Atomic Scale Using Scanning Tunneling Microscopy and Spectroscopy," P. S. Weiss, Boston, MA, August 20, 1999.

American Vacuum Society 46th International Symposium, "How Low Can You Go with Scanning Probe Microscopy?" P. S. Weiss, Seattle, WA, October 26, 1999.

American Vacuum Society 46th International Symposium, "Controlling the Placement of Molecules in the Self Assembly and Directed Assembly of Organic Monolayers," P. S. Weiss, D. L. Allara, L. A. Bumm, and J. J. Jackiw, Seattle, WA, October 28, 1999.

University of Akron, Department of Physics, "Vibrational Spectroscopy of Single Molecules with the Scanning Tunneling Microscope," S. A. Kandel, Akron, OH, December 2, 1999.

i. *Submitted presentations:*

1997 Annual Joint Symposium of the Delaware Valley and Greater New York Chapters of the American Vacuum Society, "Transient Mobility and Step Edge Effects on Benzene Adsorption on Ni{110}," J. H. Ferris, J. G. Kushmerick, J. A. Johnson, and P. S. Weiss, Piscataway, NJ, June 4, 1997. Poster presented by J. H. Ferris.

57th Annual Conference on Physical Electronics, "Interactions and Dynamics of Adsorbed Aromatic Molecules and Radicals," P. S. Weiss, M. M. Kamna, and T. M. Graham, Eugene, OR, June 20, 1997.

STM'97, 9th International Conference on Scanning Tunneling Microscopy, "Imaging Adsorbed and Their Interactions with Scanning Tunneling Microscopy," M. M. Kamna, T. M. Graham, and P. S. Weiss, July 22, 1997, Hamburg, Germany. Poster.

STM'97, 9th International Conference on Scanning Tunneling Microscopy, "Imaging and Probing Self-Assembled Monolayers and Molecules Inserted in These Organic Films," L. A. Bumm, J. J. Arnold, M. T. Cygan, J. D. Shore, L. F. Charles, T. D. Dunbar, D. L. Allara, L. Jones, T. P. Burgin, J. M. Tour, and P. S. Weiss, July 23, 1997, Hamburg, Germany.

58th Conference on Physical Electronics, "Control of Self-Assembled Monolayer Film Structure and Properties," L. F. Charles, L. A. Bumm, J. J. Jackiw, J. A. Johnson, E. H. Muth, T. D. Dunbar, D. L. Allara, and P. S. Weiss, University Park, PA, June 16, 1998. Poster presented by Lyndon Charles.

58th Conference on Physical Electronics, "Atomic-Scale Insight into Catalytic Promoters," J. G. Kushmerick and P. S. Weiss, University Park, PA, June 16, 1998. Poster presented by James Kushmerick.

American Chemical Society, Colloid and Surface Section Meeting, "Patterning Molecules on the Nanometer Scale," L. A. Bumm, J. J. Arnold, L. F. Charles, M. T. Cygan, T. D. Dunbar, D. L. Allara, and P. S. Weiss, University Park, PA, June, 1998. Presented by L. A. Bumm.

216th Meeting of the American Chemical Society, "Atomic-Scale Insight into the Catalytic Properties of Nickel-Promoted Molybdenum Disulfide," J. G. Kushmerick and P. S. Weiss, Boston, MA, August 21, 1998 and August 22, 1998. Poster and Sci-Mix poster presented by J. G. Kushmerick.

American Vacuum Society 45th International Symposium, "Phenyl-Containing Radicals on Cu{111}," G. S. McCarty, M. M. Kamna, and P. S. Weiss, Baltimore, MD, November 2, 1998. Poster presented by G. S. McCarty.

American Vacuum Society 45th International Symposium, "Control of Self-Assembled Monolayer Film Structure and Properties," P. S. Weiss, L. F. Charles, L. A. Bumm, T. D. Dunbar, and D. L. Allara, Baltimore, MD, November 3, 1998. Presented by L. F. Charles.

American Vacuum Society 45th International Symposium, "Growth, Modification, and Control of the Structures of Mixed Composition Organic Monolayers," T. D. Dunbar, T. P. Burgin, J. M. Tour, D. L. Allara, and L. A. Bumm, Baltimore, MD, November 3, 1998. Presented by L. A. Bumm.

American Vacuum Society 45th International Symposium, "Controlling Defects in Self-Assembled Monolayers," J. J. Jackiw, J. J. Arnold, J. A. Johnson, T. D. Dunbar, T. L. Spiva, D. L. Allara, and P. S. Weiss, Baltimore, MD, November 4, 1998. Presented by J. J. Jackiw.

American Vacuum Society 45th International Symposium, "Tunneling and Photon Emission of Colloidal Particles," G. S. McCarty, C. D. Keating, P. S. Weiss, and M. J. Natan, Baltimore, MD, November 5, 1998. Poster presented by G. S. McCarty.

American Vacuum Society 45th International Symposium, "Anisotropic Electron Scattering from Point Defects on Graphite at Low Temperature," K. F. Kelly, J. G. Kushmerick, H. P. Rust, N. J. Halas, and P. S. Weiss, Baltimore, MD, November 5, 1998. Poster presented by J. G. Kushmerick.

1999 Centennial American Physical Society Meeting, "Electron Transport Through Organic Molecules," L. A. Bumm, L. F. Charles, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, Atlanta, GA, March 24, 1999. Presented by L. A. Bumm.

STM '99: the 10th Scanning Tunneling Microscopy Conference, "Identifying and Locating Functional Groups by Selective Reactions: Staining for Scanning Probe Microscopy," G. S. McCarty and P. S. Weiss, Seoul, Korea, July 19, 1999.

American Chemical Society Meeting, "Directing Assembly in Monolayers by Controlling Solution Exchange Kinetics," A. L. Bross,* A. Hooper, D. L. Allara, and P. S. Weiss, New Orleans, LA, August 22, 1999.

*Winner of the I. M. Kolthoff Award for Undergraduate Research in Analytical Chemistry.

American Chemical Society Meeting, "Differentiating Molecular Structures in Scanning Tunneling

Microscopy," G. S. McCarty, C.D. Keating, D.J. Fuchs, and P. S. Weiss, New Orleans, LA, August 23, 1999.

j. *Honors/Awards/Prizes for contract/grant employees:*

Jamie J. Arnold
Eberly College of Science Roberts Award.

Aimee L. Bross
Eberly College of Science John and Elizabeth Teas Scholarship.
American Chemical Society, Analytical Chemistry Division, I. M. Kolthoff Undergraduate Research Award.
American Physical Society, Chemical Physics Division, Graduate Student Travel Award.

Michael T. Cygan
National Research Council Post-doctoral Fellowship (for the Naval Research Laboratory)

Terrence G. D'Onofrio
Roberts Graduate Research Award

James H. Ferris
Dorothy M. Hoffman Vacuum Education Award, 2nd Prize.

Marilyn M. Kamna
Eberly College of Science Roberts Award.

James G. Kushmerick
Twelfth Graduate Research Exhibition, Honorable Mention.
Braddock Graduate Fellowship of the Eberly College of Science.

Greg S. McCarty
American Vacuum Society, Nanometer Science and Technology Division Travel Award.
Lubrizol Graduate Research Award, 1999

Elizabeth Muth
Eberly College of Science John and Elizabeth Teas Scholarship.

Stephan J. Stranick
Ithaca College Young Alumnus of the Year.

Roger Wang
College of Engineering H. Thomas and Dorothy Willits Hallowell Scholarship.
The Pennsylvania State University Presidential Freshman Award.

Paul S. Weiss
Guest Editor for Special Issue of *Israel Journal of Chemistry*.

John Simon Guggenheim Memorial Fellowship.
Visiting Professor, Department of Molecular Biotechnology, University of Washington.
National Science Foundation Special Creativity Award.
Visiting Professor, Department of Electronic Science and Engineering and the Venture Business
Laboratory, Kyoto University.
Elected Fellow, American Association for the Advancement of Science.

Final Report - PART II

- a. *Principal Investigator*
Paul S. Weiss
- b. *Current telephone number*
(814) 865-3693 voice
(814) 863-5516 fax
- c. *Cognizant ONR Program Officer*
Dr. John C. Pazik
- d. *Program objective*

The objective of this program was to examine the electronic and physico-chemical properties, the stability, and the dynamics of nanometer-scale structures and of components that may be used in such structures. These structures and components may play key roles in evolving or even revolutionizing devices for communications, sensors, and detectors. Our understanding of these structures is developed using unique scanning tunneling microscopy instrumentation which gives us the ability to work at low temperatures, to manipulate surface structures, and to probe both electronically and over a broad frequency range. We collaborate with key developers of molecules, films, and devices to screen and to advance the properties of the components, structures, and films they create. This work serves as the scientific backbone of the technological advances in related DARPA Moletronics work and in a wide range of other areas.

- e. *Most significant results*

We have learned to manipulate defects, domains, crystallinity, desorption, exchange, insertion, grafting, conductance, and deposition to advantage in order to manipulate film structures and properties and to isolate molecules for use, study, and/or reaction.¹⁻⁸ We have used scanning tunneling microscopy, X-ray photoelectron spectroscopy, and infrared spectroscopy to measure the resultant films.

We have enhanced our abilities to measure with sub-nanometer resolution across a broad spectral range.⁸⁻¹¹ We have discovered unique opportunities at this scale, such as "optically hot" asperities on asymmetric nanoparticles. We expect to be able to exploit these effects to advantage. There are no other means of studying such materials at these scales. Couplings between molecules and nanoparticles that we propose to study may pose fundamental limitations on the densities to which functional devices can be packed.

We have demonstrated our ability to discriminate between different nanostructure

compositions. We have proposed using this capability to develop selective "stains" for scanning probe microscopy in analogy to those employed in conventional light microscopy.^{9,10} The difference here is that much higher spatial resolution will be possible so that single exposed functional groups may be labeled.

Specific accomplishments relating to the above are:

Selecting the separation or mixing of components at the nanometer scale.^{4,7} In addition, we can graft one film onto another in two dimensions. This enables selective decoration or reaction of unique surface sites at an interface that is physically perfect, but chemically distinct from the rest of the surface.^{4,7}

Selective removal of specific defects by processing films and controlling their completeness.^{1,4,7} This leads to independent control of insertion, exchange, and removal of molecules.

Insertion of single molecules for subsequent study or reaction.^{3,8,11} These molecules can then be probed individually or in bundles.^{8,11} Recent (unpublished) experiments allow us to follow electronic switching of inserted molecules. This isolation also enabled the first example of the selective chemical modification of surface species without disrupting the nanometer-scale structure.³ A living polymer was grown off inserted, isolated tethers. It was also possible to bundle together the tethers so as to select growth of surface-bound polymer brushes. These polymers and the controlled substrate on which they lie may be used to create non-volatile nanometer-scale organic memory.²

We have observed "optically hot" regions on single nanoparticles.^{9,10} These may be used to enhance spectroscopy, optical coupling at the nanometer scale, or isolation at this scale. We have also shown that nanoparticles couple electronically as they are brought into proximity, but remain out of chemical contact (not yet published). We have created a unique system for studying these interactions that does not depend on bulk synthesis and laborious separations. This will allow us to explore the phase space of these interactions and their dependence on separation and orientation, before targeting selected assemblies for synthesis.

Our ONR Program has served as the core for discovery in our group, from which a large number of other efforts have emanated.

¹*Directing Assembly in Monolayers by Controlling Exchange Kinetics*, A. L. Bross, A. E. Hooper, L. A. Bumm, D. L. Allara, and P. S. Weiss, to be submitted to *Journal of Physical Chemistry B*.

² *Strong Substrate Effect in Local Poling of Ultrathin Ferroelectric Polymer Films*, X. Q. Chen, Y. Terai, T. Horiuchi, H. Yamada, K. Matsushige, and P. S. Weiss, *Thin Solid Films* **353**, 259 (1999).

³*Ring-Opening Metathesis Polymerization from Surfaces*, M. Weck, J. J. Jackiw, R. R. Rossi, P. S. Weiss, and R. H. Grubbs, *Journal of the American Chemical Society* **121**, 4088 (1999).

⁴*Directed Self-Assembly to Create Molecular Terraces with Molecularly Sharp Boundaries in Organic Monolayers*, L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, *Journal of the American Chemical Society* **121**, 8017 (1999).

⁵*Electron Transport through Organic Molecules*, L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, *Journal of Physical Chemistry B* **103**, 8122 (1999).

⁶*Molecular Caltrops: Adsorption and Spectroscopy*, A. Hatzor, P. Harder, G. S. McCarty, D. J. Fuchs, J. M. Tour, D. L. Allara, and P. S. Weiss, to be submitted.

⁷*Creating, Tailoring and Using One-Dimensional Interfaces in Two-Dimensional Films*, P. S. Weiss, H. Yokota, R. Aebbersold, G. van den Engh, L. A. Bumm, J. J. Arnold, T. D. Dunbar, and D. L. Allara, *Journal of Physics: Condensed Matter* **10**, 7703 (1998).

⁸*Insertion, Conductivity, and Structures of Conjugated Organic Oligomers in Self-Assembled Alkanethiol Monolayers on Au{111}*, M. T. Cygan, T. D. Dunbar, J. J. Arnold, L. A. Bumm, N. F. Shedlock, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, *Journal of the American Chemical Society* **120**, 2721 (1998).

⁹*Scanning Tunneling Microscopy and Spectroscopies of Nanometer-Scale Particles*, G. S. McCarty, J. C. Love, J. G. Kushmerick, L. F. Charles, C. D. Keating, B. J. Toleno, M. E. Lyn, A. W. Castleman, Jr., M. J. Natan, and P. S. Weiss, *Journal of Nanoparticle Research* **1** (1999), in press.

¹⁰*Scanning Probe Studies of Single Nanostructures*, G. S. McCarty and P. S. Weiss, *Chemical Reviews* **99**, 1983 (1999).

¹¹*Are Single Molecular Wires Conducting?* L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, *Science* **271**, 1705 (1996).

- g. *List of names of graduate students and post-doctorals who worked on the project*

Jamie J. Arnold, Lyndon F. Charles, Michael T. Cygan, Terrence G. D'Onofrio, Jennifer J. Jackiw, Jennifer J. Johnson, James G. Kushmerick, Kyle R. Krom, Marilyn M. Kamna, Greg S. McCarty, and James Shore (others in prior funding periods).

Dr. Lloyd A. Bumm, Dr. Michael T. Cygan, Dr. S. Alex Kandel, and Dr. Kevin F. Kelly.

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 96PR00670

Contract/Grant Number: N00014-91-J-1630

Contract/Grant Title: Creation and Measurement of Components for Nanometer-Scale and Hybrid-Function Devices

Principal Investigator: Paul S. Weiss

Mailing Address:

152 Davey Laboratory

The Pennsylvania State University

University Park, PA 16802-6300

Phone Number: (814) 865-3693

Fax Number: (814) 863-5516

E-mail Address: stm@psu.edu

http address: <http://stm1.chem.psu.edu/>

- a. Number of papers submitted to refereed journals, but not published: 3
- b. + Number of papers published in refereed journals: 23
- c. + Number of books or chapters submitted, but not yet published: 0
- d. + Number of books or chapters published: 0
- e. + Number of printed technical reports/non-refereed papers: 5
- f. Number of patents filed: 0
- g. + Number of patents granted: 0
- h. + Number of invited presentations: 51
- i. + Number of submitted presentations: 18
- j. + Honors/Awards/Prizes for contract/grant employees: 22
- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported, under this R&T project number: 7
 - Graduate Students: 4
 - Post-Doctoral Associates: 3
 - including the number of,
 - Female Graduate Students: 2
 - Female Post-Doctoral Associates: 0
 - Minority* Graduate Students: 0.5
 - Minority* Post-Doctoral Associates: 0
 - Asian Graduate Students: 0
 - Asian Post-Doctoral Associates: 0